

Chapter 10

Molecular Geometry and Chemical Bonding Theory

Concept Check 10.1

An atom in a molecule is surrounded by four pairs of electrons, one lone pair and three bonding pairs. Describe how the four electron pairs are arranged about the atom. How are any three of these pairs arranged in space? What is the geometry of this atom plus the three bonded to it?

Solution

The VSEPR model predicts that four electron pairs about any atom in a molecule will distribute themselves to give a tetrahedral arrangement. Any three of these electron pairs would have a trigonal pyramidal arrangement. The geometry of a molecule having a central atom with three atoms bonded to it would be trigonal pyramidal.

Concept Check 10.2

Two molecules, each with the general formula AX_3 , have different dipole moments. Molecule Y has a dipole moment of zero, whereas molecule Z has a nonzero dipole moment. From this information, what can you say about the geometries of Y and Z?

Solution

A molecule AX_3 could have one of three geometries: it could be trigonal planar, trigonal pyramidal, or T-shaped. Assuming that the three groups attached to the central atom are alike, as indicated by the formula, the planar geometry should be symmetrical, so that even if the A—X bonds are polar, their polarities would cancel to give a nonpolar molecule (dipole moment of zero). This would not be the case in the trigonal pyramidal geometry. In this

situation the bonds all point to one side of the molecule. It is possible for such a molecule to have a lone pair which would point away from the bonds, whose polarity might fortuitously cancel the bond polarities, although an exact cancellation is not likely (see Figure 10.20). In general, you should expect the trigonal pyramidal molecule to have a nonzero dipole moment, but a zero dipole is possible. The argument for the T-shaped geometry is similar to that for the trigonal pyramidal geometry. The bonds point in a plane, but toward one side of the molecule. Unless the sum of the bond polarities was fortuitously canceled by polarities from lone pairs, this geometry would have a nonzero dipole moment. This means that molecule Y is likely to be trigonal planar, but trigonal pyramidal or T-shaped geometries are possible. Molecule Z cannot have a trigonal planar geometry, but must be either trigonal pyramidal or T-shaped.

Concept Check 10.3

An atom in a molecule has one single bond and one triple bond to other atoms. What hybrid orbitals do you expect for this atom? Describe how you arrived at this result.

Solution

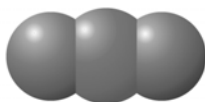
Assuming that there are no lone pairs, the atom has four electron pairs and, therefore, an octet of electrons about it. The single bond and the triple bond each require a sigma bond orbital, for a total of two such orbitals. This suggests sp hybrids on the central atom.

Conceptual Problem 10.17

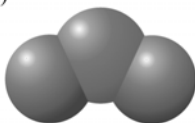
Match the following molecular substances with one of the molecular models (i) to (iv) that correctly depicts the geometry of the corresponding molecule.

a. SeO_2 b. BeCl_2 c. PBr_3 d. BCl_3

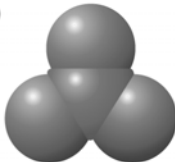
(i)



(ii)



(iii)



(iv)



Solution

In order to solve this problem, draw the Lewis structure for each of the listed molecules. In each case, use your Lewis structure to determine the geometry and match this geometry with the correct model.

- SeO_2 is angular and has an AB_2 geometry. This is represented by model (ii).
- BeCl_2 is linear and has an AB_2 geometry. This goes with model (i).
- PBr_3 is trigonal pyramidal and has an AB_3 geometry. This goes with model (iv).
- BCl_3 is trigonal planar and has an AB_3 geometry. This is represented by model (iii).

Conceptual Problem 10.18

Which of the following molecular models correctly depicts the geometry of ClCN ?



Solution

First, determine the geometry about the central atom, carbon. There is a total of sixteen valence electrons for the molecule. For each atom to obey the octet rule, eight electrons must be shared in bonds. This would require four bonding pairs, a single bond (one pair) between C and Cl, and a triple bond (three pairs) between C and N. The geometry about the central atom is AX_2 , which is linear. This is represented by model (a), on the left.

Conceptual Problem 10.19

Suppose that an ethane molecule, CH_3CH_3 , is broken into two CH_3 molecules in such a way that one $:\text{CH}_3$ molecule retains the electron pair that was originally the one making up the $\text{C}-\text{C}$ bond. The other CH_3 molecule has two fewer electrons. Imagine that momentarily this CH_3 molecule has the geometry it had in the ethane molecule. Describe the electron repulsions present in this molecule and how they would be expected to rearrange its geometry.

Solution

In a CH_3CH_3 molecule, each C atom has four electron pairs arranged tetrahedrally. Within this molecule, each CH_3 considered as a separate group has a trigonal pyramidal geometry (with three $\text{C}-\text{H}$ bonding pairs and a fourth pair from the $\text{C}-\text{C}$ bond around the C atom). The $:\text{CH}_3$ molecule retains this trigonal pyramidal geometry, having three bonding pairs and one lone pair around the C atom. The CH_3 molecule, however, has only three electron pairs around the C atom. Initially, as the CH_3 molecule breaks away from the ethane molecule, it

has the trigonal pyramidal geometry it had in the ethane molecule. However, the repulsions of the bonding electron pairs on the CH_3 molecule are no longer balanced by the fourth pair (from the C—C bond), so the molecule flattens out to form a trigonal planar geometry.

Conceptual Problem 10.19

What are the bond angles predicted by the VSEPR model about the carbon atom in the formate ion, HCO_2^- ? Considering that the bonds to this atom are not identical, would you expect the experimental values to agree precisely with the VSEPR values? How might they differ?

Concept Target

- Note how slight differences in sizes of bonding pairs affect bond angles predicted by the VSEPR model.

Solution

The formate ion, HCO_2^- , is expected to have trigonal planar geometry by the VSEPR model. (Each resonance formula has one C=O bond, one C—O bond, and one C—H bond, giving a total of three groups about the C atom.) The VSEPR model predicts bond angles of 120° . However, a bond between the carbon atom and an oxygen atom has a bond order of $3/2$ (resonance between a single and a double bond) and requires more room than a pure single bond. The repulsion between the two C—O bonds would be greater than the repulsion between a C—O bond and the C—H bond. Thus, you would predict that the O—C—O angle is slightly greater than 120° , whereas an O—C—H angle is slightly less than 120° .

Conceptual Problem 10.20

Suppose that a BF_3 molecule approaches the lone pair on the N atom of an $:\text{NH}_3$ molecule, and that a bond forms between the B atom and the N atom. Consider the arrangement of electron pairs about the B atom at the moment of this bond formation, and describe the repulsions among the electron pairs and how they might be expected to change the geometry about the B atom.

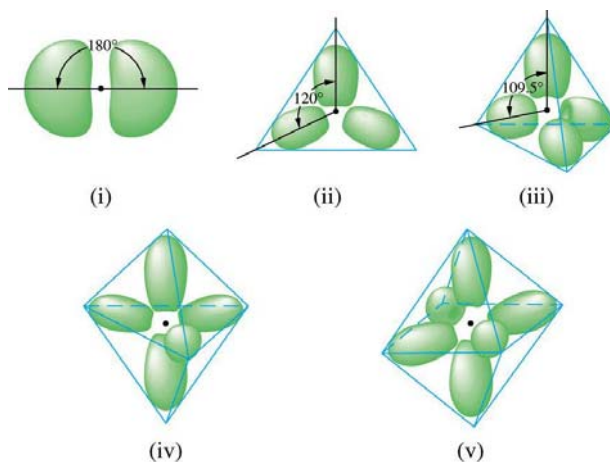
Solution

The BF_3 molecule starts out in a trigonal planar geometry with three bonding pairs of electrons distributed about the B atom in a plane and 120° apart. After the bond between B and N is formed, the geometry about the B atom is tetrahedral, with 109° bond angles. As the bond begins to form, the lone pair on N approaches the plane of the BF_3 molecule and begins to interact with the bonding pairs. The repulsion between the electron pairs causes the bonding pairs to be pushed downward, forcing them closer together.

Conceptual Problem 10.21

Match the hybrid orbitals depicted below that are expected for the central atom of each of the following:

- a. BeF_2 b. SiF_4 c. SeF_4 d. RnF_4



Solution

First, determine the geometry of each molecule using VSEPR theory. Then, compare to the orbital pictures for the correct number of bonding and nonbonding orbitals.

- BeF_2 is an AX_2 molecule, which has linear geometry. This is depicted by orbital drawing (i).
- SiF_4 is an AX_4 molecule, which has tetrahedral geometry. This is depicted by orbital drawing (iii).
- SeF_4 is an AX_4E molecule, which has seesaw geometry. This is depicted by orbital drawing (iv).

- d. RnF_4 is an AX_4E_2 molecule, which has square planar geometry. This is depicted by orbital drawing (v).

Conceptual Problem 10.22

An atom in a molecule has two bonds to other atoms and one lone pair. What kind of hybrid orbitals do you expect for this atom? Describe how you arrived at your answer.

Solution

The arrangement of electron pairs about this atom suggested by the two bonds and one lone pair is trigonal planar. You would expect sp^2 hybrid orbitals for this atom (a total of three hybrid orbitals). Two of these hybrid orbitals would be used to form the two bonds; the third hybrid orbital would be used for the lone pair.